# Application of a microbial fuel cell to treat municipal and industrial sewage for energy recovery

S. Malamis\*, K. Vlachas, A.M. Giannakou

\*Department of Water Resources and Environmental Engineering, School of Civil Engineering, National Technical University of Athens, 5 Iroon Polytechniou St, 15780, Athens Greece (E-mail: <u>smalamis@central.ntua.gr</u>)

#### Abstract

This work examined the start-up and operation of a microbial fuel cell (MFC) for the simultaneous wastewater treatment and energy retrieval from raw sewage, primary effluent and cheese whey, using di fferent to (oxygen, nitrate, sulfate) and aeration system (diffuse aeration, passive aeration). The main aim was to evaluate the MFC's e fficiency

design (H-type) was based on inexpensive materials. The COD removal efficiency accomplished by the MFC was 75-90% for total COD and 70-75% for soluble COD. All cycles, in which raw sewage and primary effluent were used, accomplished the COD concentration limit set by Directive 91/271/EEC of 125 mg/l at the end of the cycle. Comparing the different aeration methods, diffuse aeration achieved 75% COD removal, while passive aeration accomplished 70%. In terms of energy recovery, MFC technology managed to reach, in the case of raw sewage with diffuse aeration, on average 107 Wh/kg COD<sub>removed</sub> which is higher than the usual values found in literature (70-90 Wh/kg COD<sub>removed</sub>). Cycles with passive aeration resulted in lower energy recovery in the range of 25-45 Wh/kg COD<sub>removed</sub>. When industrial wastewater with high organic content was applied as substrate, the MFC could effectively remove COD under both passive aeration.

#### Keywords

Microbial fuel cell, municipal wastewater, cheese whey, energy recovery, passive aeration, sulphate, nitrate

#### Introduction

A Microbial Fuel Cell (MFC) is defined as a technology, through which the reserved chemical energy of wastewater is converted to electrical energy, using the catalytic reactions of microorganisms under anaerobic conditions. This technology possesses a twofold nature, since it can simultaneously treat wastewater and produce electricity. For that reason, it has gained increasing interest amongst the scientific and research community, over the last years. In this work, the start-up and operation of MFC technology, concerning the simultaneous wastewater treatment and energy retrieval from municipal wastewater and cheese way, was examined in a dual chamber MFC design, known as H-type MFC. (Logan, 2008; Du et al., 2007)

This work examined different type of wastewater (raw sewage, primary effluent and cheese whey effluent), different aeration mode (passive, diffuse) and electron acceptors (oxygen, nitrate, sulphate). The main goal was to examine the start-up and development of the biofilm on the anode electrode, the evaluation of the MFC's efficiency in terms of wastewater treatment and simultaneous energy recovery and the comparison of the research results to the efficiency of conventional wastewater treatment plants (WWTPs). This approach was made with the objective of the potential practical application of MFCs in WWTPs by replacing the activated sludge process.

#### Material and methods

The development of the dual chamber MFC design (H-type) was based on the use of inexpensive material and the configuration of parameters in a way that they resembled the actual environmental conditions. The architecture of the reactor included two chambers, the anode and the cathode, the volumes of which were 300 ml respectively (Ieropoulos et al., 2008). The two chambers were connected through a glass tube of 8 cm length and 1.5 cm internal diameter, forming the H-type reactor. A Nafion Proton Exchange Membrane

of 0.125 mm width and 3.8 cm<sup>2</sup> total surface was placed inside the tube, in order to ensure the electrolytic connection. The anode and the cathode electrodes were Teflon-treated-carbon plates, 4 cm x 2.9 cm x 0.9 cm, with an active surface of 31.7 cm<sup>2</sup> each (4x2.9 cm<sup>2</sup>). The two electrodes were placed vertically, with their bigger surfaces facing one another, in a total distance of 5.5 cm. The two electrodes were externally connected with titanium wires and an electrical resistance of 10 k $\Omega$  in order to form the electrical circuit. A digital voltmeter was attached in the circuit in order to measure the voltage in the resistance and the amount of the consumed electrical energy.

During the period of experimentation 26 cycles were carried out, separated in two phases. First, an inoculation stage preceded in order to grow/cultivate biofilm on the anode electrode. The MFC system was operated in batch mode, with the anode solution consisting of 20 ml (7%) digested sludge and 280 ml (93%) sewage. Substrate (sodium acetate) was periodically added to the anode in order to achieve an initial concentration of 1 gr COD/l in the anodic solution, with the objective of promoting the development of the biofilm and ultimately, boosting the biochemical reactions.

The first phase of experimentation included 12 cycles and the MFC system was operated in batch mode, using different types of sewage, while the cathode chamber operated under aerobic conditions with diffuse aeration. Specifically, the electron donors used in the MFC system were primary effluent (5 cycles), subsequently raw sewage (4 cycles), and, finally, cheese whey for 3 cycles.

In the 14 cycles of the second phase that followed, different types of electron acceptors and aeration conditions were applied in the cathode chamber to treat raw sewage and primary effluent. More specifically, oxygen was used as electron acceptor for the first 4 cycles, with the cathode chamber operating under aerobic conditions with diffuse aeration. The first 2 of these 4 cycles were run with raw sewage and the next 2 with primary effluent. Subsequently, the cathode chamber continued to operate under aerobic conditions, but with passive aeration for 8 cycles in total. During the first 6 of these cycles, nitrate (solutions of KNO<sub>3</sub>  $\kappa \alpha t$  NaNO<sub>3</sub>) was added in the cathode with raw sewage as electron donor for 3 cycles and primary effluent for another 3. Then, for the next 2 cycles, sulphate was added using solutions of sulphate salts as electron acceptor respectively.

Due to oxygen penetration in the cathode chamber in the passive aeration configuration, oxygen was the main electron acceptor. Further experiments were carried out through a purging procedure where nitrogen was supplied to the cathode, to ensure that oxygen in the cathode was replaced with inert nitrogen and did not operate as an electron acceptor. As a result, the MFC system was tested in operation with nitrate and sulphate alone as electron acceptor in the cathode. Thus, the anoxic/anaerobic conditions in the cathode chamber signified the last 3 cycles of the phase, 2 with nitrate as electron acceptor and 1 cycle with sulphate. In these final 3 cycles, raw sewage was used as electron donor and sodium acetate was added as a substrate to ensure the high concentration of organic matter in the anode that would help observing the decrease of the electron acceptor.

## **Results and discussion**

The tests that were performed during all the cycles were related to the parameters that can influence the efficiency of the MFC system. The investigation of the MFC performance focused, in terms of wastewater treatment, on the removal of total and soluble COD, the required hydraulic retention time (HRT) for attaining the treated effluent COD limit specified by European Directive 91/271/EEC, the removal of total suspended solids (TSS) and volatile suspended solids (VSS), the fate of ammonium nitrogen and phosphate and the fluctuation of pH. In terms of recovered energy, the examined parameters were the electrical power and energy per mass of COD removed (W/Kg COD και Wh/Kg COD) and per volume of the anode chamber (W/l και Wh/l), and were calculated using the voltage that the system produced. Additionally, after the end

of each phase of the experimental cycles, a microscopic observation of the biofilm of the anode's electrode was conducted, in order to identify the microorganisms that had grown on its surface.

During the first phase of experimentation, the COD removal efficiency accomplished by the MFC was 80-90% for total COD and 70-75% for soluble COD (Table 1). The accomplished removal efficiency in terms of total COD was the same when raw sewage and primary effluent were used as electron donors, whereas the soluble COD removal turned out to be 10% higher when raw sewage was used. All cycles in which raw sewage or primary effluent were used, managed to achieve the COD concentration limit set by Directive 91/271/ECC of 125 mg/l. On the contrary, the removal of TSS and VSS, was lower and ranged between 50-60%. The average HRT required to accomplish the aforementioned COD removal was 35 and 82 hours for primary effluent and raw sewage respectively. Given the very high HRT, significant operational improvement of MFC is required in order to be competitive.

In the last 3 cycles where cheese whey was used, the COD removal efficiency accomplished by the MFC was 80-85% for total COD and 85-89% for soluble COD. In addition, the average HRT was 15-20 days. During these 3 cycles the pH was occasionally adjusted to the neutral values of 7-8 so that the conditions in the anode chamber were beneficial for the chemical reactions that took place.



Figure 1. Total and soluble COD in the anode chamber and voltage in the MFC for the treatment of raw sewage.

Figure 1 shows the variation of total and soluble COD in the anode chamber and voltage in the MFC for the treatment of raw sewage. Initially, a steep increase of voltage was observed together with a steep decrease of COD concentration in a short time. Then, the voltage exhibited a slow increase and even stable values at times, while the organic load gradually decreased as expected. Towards the end of the cycle once the biodegradable COD had been depleted, a rapid decrease of voltage was observed.

In terms of energy recovery, as shown in Table 1, the cycles with raw sewage as electron donor, resulted in the highest rate of energy and power per mass of COD removed and per volume of the anode chamber. When primary effluent was used as substrate, the average energy recovery was  $0.38 \text{ Wh/l}_{reactor}$  in terms of

anodic chamber volume and 34 Wh/kg  $COD_{removed}$ . These rates are slightly lower than the average rate of 50-60 Wh/kg  $COD_{removed}$  that is met in literature. The energy recovery with raw sewage was 0.06 Wh/l<sub>reactor</sub> and 107 Wh/kg  $COD_{removed}$  respectively, which are slightly more effective than the average rate of 70-90 Wh/kg  $COD_{removed}$  met in literature. The energy rates that were achieved during the cycles when cheese whey was used were low. Specifically, the average energy recovery was 4.25 Wh/kg  $COD_{removed}$  respectively. It is essential to point out that the results of this work in terms of energy recovery have been achieved without chemical adjustment of the initial parameters (for example: without catalysts or using municipal sewage instead of a pure chemical substrate as electron donor).

	HRT (d) -	COD removal (mg/l)		Energy recovery	
		Total	Soluble	Wh/kg COD	Wh/l
Raw sewage as electron donor	3.42	86%	79%	107	0.06
Primary effluent as electron donor	1.46	85%	69%	34	0.038
Cheese whey as electron donor	27	83%	87%	4.25	

**Table 1**. MFC performance in terms of required HRT, COD removal and energy recovery for different types of aeration conditions (average value over the cycles are given for each parameter).

The experiments that were conducted during the second phase, focused on the comparison between different electron acceptors and aeration conditions in the cathode chamber. The main results are presented on Table 2. The average total COD removal of all cycles was approximately 75% and the soluble COD removal around 50%. Simultaneously, in 8 out of 12 cycles managed the COD limit of 125 mg COD /l was accomplished, while almost all cycles managed to achieve a removal higher than 75%. Comparing the different electron acceptors, oxygen provided with diffuse aeration achieved an average removal efficiency of total COD around 75% at an average HRT of 6.5 days, while in cycles where passive aeration was used in the cathode, the COD removal efficiency dropped to 70%. The last 3 cycles during which the cathode chamber was purged of oxygen, were an exception to the rule. Due to the unstable nature of the experiments during these cycles and also to the fact that oxygen was not fully removed from the cathode, the results of these 3 cycles were ambiguous, and unable to lead to a secure conclusion. Moreover, a particularly low removal of sulfate and nitrate which were used as electron acceptors was observed. Specifically, a removal rate of 15% for nitrate and 7% for sulfate was achieved in the cathode, indicating passive aeration conditions since COD was removed. The low removal rates were due to the presence of oxygen in the cathode chamber, which made it the main electron acceptor, thus restricting the biochemical reactions of nitrate and sulfate removal in the cathode.

	HRT (d)	COD removal (mg/l)		Energy recovery	
		Total	Soluble	Wh/kg COD	Wh/1
Oxygen under aerobic conditions	6.5	75%	65%	60	0.023
Nitrate under passive aeration	5	73%	50%	24	0.008
Sulfate under passive aeration	4.5	70%	52%	45	0.013

**Table 2**. MFC performance in terms of required HRT, COD removal and energy recovery for different types of aeration conditions (average value over the cycles are given for each parameter).

In terms of energy recovery, the cycles with diffuse aeration developed the highest recovery of energy and power per mass of COD removed and per volume of the anode chamber. In the first cycles, where oxygen worked as the electron acceptor under aerobic conditions with diffuse aeration, the energy recovery was 0.023 Wh/l in terms of anodic chamber volume and 60 Wh/kg COD in terms of COD removal. When passive aeration with the presence of nitrate in the cathode was used, the respective results were 0.008 Wh/l and 24 Wh/kg COD. Finally, the cycles with passive aeration and the presence of sulfate achieved an energy efficiency of 0.013 Wh/l and 45 Wh/kg COD. The energy efficiency rates that oxygen could provide when used as an electron acceptor seem to be as competitive as similar rates met in literature that vary between 50-60 Wh/kg COD removed. It is also noticed that the presence of even small concentrations of oxygen does not allow other nitrate/sulphate to be used as electron acceptors, since their concentration removal in the cathode chamber is particularly low.



**Figure 2.** Diagrammatic identification of the microorganisms' cultivations in the biofilm of the electrode in the anode chamber.

Finally, an identification of the microorganisms' cultivations in the biofilm of the electrode in the anode chamber was carried out by the end of the experiment. In the biofilm,  $\alpha$ -,  $\beta$ -, and  $\delta$ - proteobacteria, were identified with the latter being the dominant species, whereas archaea were not found. A more detailed diagram can be found above, in Figure 2.

# Conclusions

This work shows that MFC technology can be effectively applied to treat municipal and industrial (cheese whey) wastewater. The removal efficiency of COD achieved and the energy recovered were relatively higher than the usual values found in literature. Moreover, the potential of the MFC technology in terms of wastewater treatment was proved, not only in liquid urban wastewater, but also in synthetic liquid waste such as cheese whey. As far as the aeration systems that were used in the cathode are concerned, the main conclusion is that the operation of the MFC technology under passive aeration can be as effective as the one under diffuse aeration. The obtained results can be used as a guide towards the future enhancement of the MFC technology, with the objective of implementing it as part of a conventional wastewater treatment plant.

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